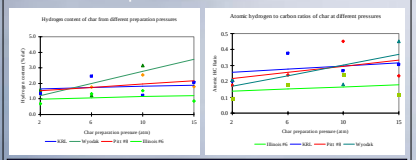
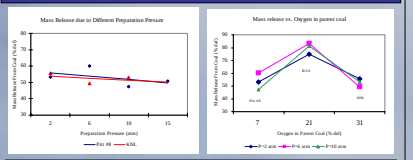
Effect of Formation Pressure on Char Properties (Cont'd)

Elemental Compositions of Chars and Mass Release Data



- Hydrogen content of chars is low enough to represent industrial conditions
- Hydrogen content of chars shows general trend of increase with char preparation pressure

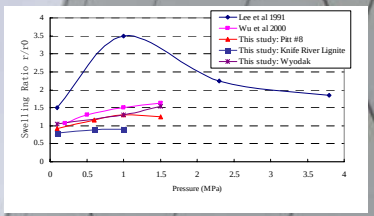


- Mass release from ash tracer, Al, and Ti tracers
- Mass release decreases as total pressure increases
- Density (not shown) decreases with increases in pressure

Comparison of Experiment Conditions of Char Swelling Ratio

	Authors		
	Lee et al.	Wu et al.	Current work
coal	Illinois No.6	Australian Bituminous coal	Three US bituminous coals and one lignite
particle size	62 μm mean particle diameter	63-90 μm	75μm average diameter
apparatus	HEF (high-pressure entrained-flow furnace)	PDTF (pressurized drop-tube furnace)	HPFFB (high-pressure flat flame burner)
heating rate	~10^4 K/s	~10^4-10^5 K/s	> 10^5 K/s
temperature	1189 K	1573 K	1573 K
pressure	0.1-3.8 MPa	0.1-1.5 MPa	0.1-1.5 MPa
atmosphere	N_2	N_2 with slightly oxidizing	Combustion product of CH_4/Air

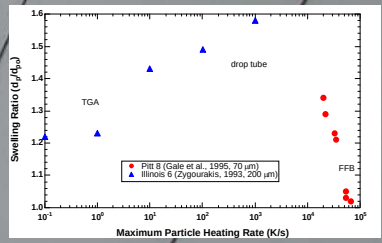
Comparison of Char Swelling Ratio Experiments



- Tap densities measured, ratio eliminates packing factor using equation $(m/m_0=(\rho/\rho_0)(d/d_0)^3$
- Swelling ratios for three coals in the HPFFB were much smaller than observed in the PDTF Shrinkage
- Increased swelling with pressure for Pitt #8 char, Wyodak char but not as much as in lower heating rate experiments

Swelling vs. Heating Rate at 1 atm

- Heating rate significantly affects swelling properties during pyrolysis of bituminous coals at atmospheric pressure (Gale et al., Comb. Flame, 1995)
- High pressure experiments at moderate heating rates may show too much swelling



Comparison of Char formation Conditions

	Authors			
	Roberts et al.[8]	Lee et al. [21]	Cai et al. [17]	This study
coal	Three Australian thermal coals	Illinois No.6 Coal	Pitt #8, Linby Coal	Pitt #8, Knife river lignite
particle size	63-90 μm	62 μm mean particle diameter	106-150 μm	75μm mean particle diameter
apparatus	PEFR (pressurized entrained-flow furnace) and PDTF (pressurized drop tube furnace)	High-pressure entrained-flow reactor	Electrically heated wire-mesh reactor	High-pressure Flat-flame burner
heating rate	~10^4-10^5 K/s	~10^4 K/s	10^3 K/s	>10^5 K/s
Pyrolysis temperature	1373 K	1189 K	973 K	1573 K
pressure	5-15 atm	100, 309, and 530 Psig	2.5-150 bar	1-15 atm
atmosphere	N_2 with stoichiometric amounts of oxygen	N_2	H_2	CH_4 combustion product (CO_2, H_2O, with 8.4% O_2)
TGA reactivity	initial reaction rate reported, 723 K	air, 683K	air, 773K	Various O_2 fraction, 693 – 753 K

Review of Published Results

Roberts et. al.
- Char oxidation reactivities of three Australian coals were measured at 10 or 15 atm at 723K in 50% O_2. One char initial reaction rate increased with pressure increase and two other chars had no clear trend.
- The reactivities after normalization by the char CO_2 surface areas were the same.

Cai and coworkers
- Both Pitt #8 and Linby char combustion reactivities decreased with hydropyrolysis pressure from low to intermediate pressure(20-30 bar), then increased with hydropyrolysis pressure

Lee et al.
- Illinois char reactivity generally decreased with increasing char formation pressure, but that this decrease was not as significant for residence times longer than 1 s
- No correlation between the micropore surface area (CO_2) of chars and reactivity

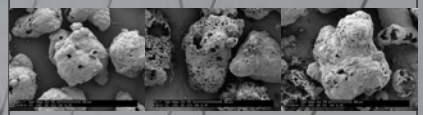
Effect of Formation Pressure on Char Reactivity

Char formation pressure affects resulting char reactivity

The effect of formation pressure on char reactivity is not fully understood

Hecker et. al. studied char high pressure oxidation using char made at 1 atm
- Same TGA analysis procedure is used to analyze char made at different pressures
- Total pressure of TGA test is kept the same as char formation pressure

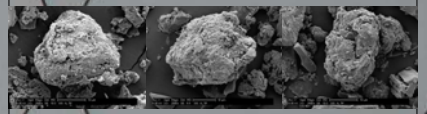
SEM Photos of Pitt #8 Chars



Pitt # 8 char (P=1 ATM) | Pitt # 8 char (P=6 ATM) | Pitt # 8 char (P=10 ATM)

- Increased pyrolysis pressure increased
  - tar precursors left in char due to vapor pressure effects
  - resistance for the volatiles to transport from the interior to the exterior
- With more volatiles retained in coal particles, char made from higher pressure showed higher fluidity
- SEM photos of char made from HP-FFB, medium pressure (6 atm) showed popped bubbles
- The 10 atm char showed fewer distinct large holes.

SEM Photos of Knife River Lignite Chars

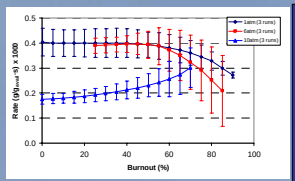


KRL char (P=1 ATM) | KRL char (P=6 ATM) | KRL char (P=10 ATM)

- No clear effect of pressure for this coal
- Effects of char formation pressure on morphology greatest for bituminous coals

Pitt 8 TGA Reactivity Data

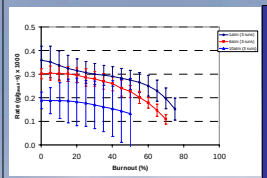
(3-5 mg samples, P_{tot} = char formation pressure)



- Pitt # 8 char (P_{O2} = 0.32 atm; T = 715 K)
- TGA (intrinsic) reactivity relatively constant until 60% burnout
- Only late burnout reactivity changes for high pressure char

Lignite TGA Reactivity Data

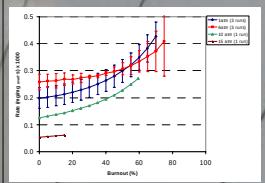
(3-5 mg samples P_{tot} = char formation pressure)



- Lignite reactivity much higher than Pitt 8, so TGA temperature lowered to get intrinsic rates
- Knife River lignite char (P_{O2}=0.28 atm; T=615 K)
- TGA (intrinsic) reactivity not constant like the Pitt 8 char
- High pressure char has 15% lower reactivity at these conditions

Illinois #6 TGA Reactivity Data

(3-5 mg samples P_{tot} = char formation pressure)



- Illinois #6 reactivity comparable to Pitt #8, so similar conditions used
- Illinois #6 (P_{O2}=0.40 atm; T=693 K)
- Char reactivity appears to decrease with increasing char preparation pressure

Pitt#8 Char Activation Energy and Oxygen Order versus Total Pressure

Total Pressure (atm)	Activation Energy (kcal/mol)	Oxygen Order	N_2 Area m^2/g
1	29.2	0.78	40
6	18.9	0.64	88
10	32.4	0.74	93
15	30.9	0.73	77

n^{th} Order kinetic models

$$-r_c = A \cdot \exp\left(-\frac{E}{RT}\right) \cdot P_{O2}^{\ n}$$

*Char formation pressure = TGA pressure, based on 3 data points